Fluoro-sensing applied to detection and identification of hydrocarbons in inland waters.

Study of the impact of different UV light sources

F. José Arqués Orobón / Vicente González Posadas / José Luis Jiménez Martín.
Dept. of Audiovisual and Communications Engineering
EUIT de Telecomunicación
Technical University of Madrid
Campus Sur. Ctra. De Valencia, km 7
28031 Madrid, Spain
fjarques@diac.upm.es

Julio Gutiérrez Ríos / Angel Esteban Orobio
Photonics Technology Dept.
Facultad de Informática.
Technical University of Madrid
Campus Montegancedo. Ctra. De Valencia, km 7
28660 Boadilla del Monte (Madrid), Spain
jgr@fi.upm.es

Abstract— **This paper presents the detection and identification of hydrocarbons through fluoro-sensing by developing a simple and inexpensive detector for inland water, in contrast to current systems, designed to be used for marine waters at large distances and being extremely costly. To validate the proposed system, three test-benches have been mounted, with various UV-light sources. Main application of this system would be detect hydrocarbons pollution in rivers, lakes or dams, which in fact, is of growing interest by administrations.**

I. INTRODUCTION

Continuous measurement of parameters in inland waters to identify their level of quality has become a necessity in today's society given the movement by diversions, dams accumulation, use, treatment and contributions of dumpings take place in the rivers. Thanks to technological development in different areas (electronics, sensors, processors and communications), has made possible the real-time monitoring of parameters such as temperature, conductivity, dissolved oxygen and pH, to name a few. Monitoring of these parameters, together with the inclusion of the context of the water reservoir, geological area, season, etc., contributes to the study, development and quality control of rivers.

A second step in this area has been providing continuous analyzers with a higher level of complexity. Within this group can be mentioned analyzers ammonium nitrate [1] and biological oxygen demand (BOD) by indirect methods.

There are parameters of the water, cited above, which, in most cases must be found within margins permissible taking into account the source of water, weather or other environmental factors. Overcoming these margins by plus or minus, as contributions undue, excessive growth of algae (eutrophication) or others, should be monitored so as not to cause a chain reaction of undesirable events, such as high mortality fish or widespread poisoning of the fish population.

Another fact that damages the quality of the rivers is referred to the presence of pollutants, which due to its hazard, should never be present, such as hydrocarbons (Figure 1.). Therefore detection and control becomes is a basic need.

Figure 1. Warning due to danger for contamination by hydrocarbon transport

Surveillance works carried out by the rivers guards are essential for proper water control. However, if spills occur after hours, the response time increases and the cleanup and control become much more complex and difficult (Figure 2.).

Figure 2. Containment efforts in the waters of the Tagus River: oil spill from thermal plant in Aceca (Toledo). August 2000. Source: Portal Hispagua (CEDEX)

These dumpings are caused by multiple reasons, since these compounds are currently present in production of energy, combustion engines in vehicles, distribution processes for various uses such as heating, etc., being susceptible therefore accidentally end up in rivers and other water sources, causing significant ecological damage.

All this requires a hydrocarbon identification method in fresh waters within the philosophy of previous analyzers: robustness, simplicity, continuous measurement capability, and lower cost than the existing to marine waters, which are targeted to localize and detect at long distances and large quantities. The scientific community extols benefits of fluoroscopy technology applied to the detection of hydrocarbons [2].

In this regard, our group has developed a device to detect fuel in marine waters (Figure 3.) based on nitrogen laser at 337nm [3]. The mounting is based on three main elements:

- Nitrogen laser at 337nm.
- Photomultiplier.
- Processor whit a high sampling rate.

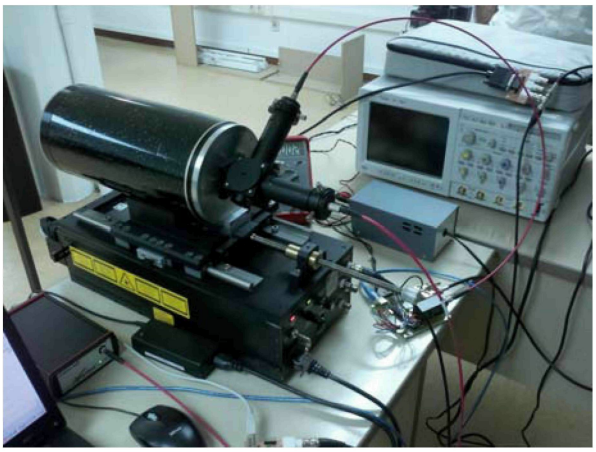


Figure 3. Device developed to oil detection in marine environment.

Due to the success of the mentioned above, combined with the lack of developments focused in inland waters, we are encouraged with the experience gained, to implement a prototype with the requirements explained.

II. FLUORESCENCE

A. *Physical phenomenon*

Photoluminescence occurs when a substance is excited by electromagnetic radiation, passing an excited electronic state. This absorption of energy can be dissipated subsequently in two different ways: (1) in the form of heat through collisions between neighboring atoms or molecules, such as occurs in the absorption spectrophotometry.

$$X + h\nu \rightarrow X^* \rightarrow X + hot \quad (1)$$

(2) In the second way, unlike the former, one part of the absorbed energy is lost as heat, and the rest is emitted as electromagnetic radiation at a different wavelength from the source.

$$X + h\nu \rightarrow X^* \rightarrow X + hot + h\nu' \quad (2)$$

Photoluminescence is defined as the emission process radiation due to the deactivation of a given molecule. Also it may happen that no excitation light energy, causing another type of luminescence called chemiluminescence, where the excitation energy comes from a chemical reaction, or if it occurs in a living being, is called bio-luminescence.

In the latter case, there are developments in this sense for detecting cyanobacteria (understanding them as pollutants). In turn, micro-algae also have a strong bio-luminescence, and currently its density in non-current water (dams and lakes) is controlled.

In regard to the substances to be analyzed and in our specific case, each of which must be characterized by its emission spectrum. Here, we observe the energy emitted by the molecules as a result of the previous process of excitation and absorption, the latter being specific for each substance.

Previous studies in this direction have been made to detect dumping in the marine environment [5][6][7][9], but as has been noted above, are used in long distances with a very powerful light source in order to obtain operative results [10][11]. However, there is little development of this kind to real-time measurement of hydrocarbons in inland waters, mainly rivers and reservoirs. The facts, however, show that periodic pollution episodes occur also in inland waters, with disastrous consequences. To introducing a system like the above is feasible, its implementation should be possible with a simple, economical, reliable and allows real-time control.

B. *Light Sources*

To produce the effect of fluorescence, it is necessary that the substance to be detected emits at a wavelength greater than the light source used, which usually works in the near ultraviolet [4][5].

To identify these contaminants through fluorodetector at a distance is necessary to know the fluorimetric response thereof. It is expected that these responses are virtually identical irrespective of the emitting source, whenever are within a range of wavelengths. However, firstly it is necessary to the development of the device described above, perform the necessary checks with light sources that are to be used to observe and store the spectra obtained at different environmental conditions.

In contrast to other studies where laser light sources are proposed, which typically emit in the near ultraviolet using nitrogen lasers, with advantages such as high output power, allowing to make measurements over long distances and with very good results, here we seek a light source that allows the development of patterns of the most common contaminants, for

short distances. For this, the source must emit at a similar wavelength to the aforementioned laser, thus ensuring good results. At the same time as it does not need so large distance ranges, the power required is lower. Transmit around 350nm ensures good results [7], existing commercial light bulbs that have a enough light intensity and low cost.

For the measurements presented in this article, and the desire to assess firsthand the distinct patterns obtained from fuel samples, measurements were taken with three different light sources:

- A conventional light bulb source (type "black light"), emitting at 365 nm (Figure 4.). These devices are fairly inexpensive compared to other sources, but with several restrictions, such as the inability to take measurements of lifetime or decay, that is, control the time at which the substance remains in the excited state before returning to steady-state [4], since this light source cannot be modulated with a sinusoid, or with a pulsed control signal. We would think in some kind of mechanical shutter to get a strobe effect, but was ruled out, at least for the scope of this work, because it involved a too complicated apparatus and its calibration was too sensitive to the original claims.

Figure 4. Ultraviolet light bulb @ 365nm

This kind of emitter presents two additional disadvantages: they have to become hot enough before achieve nominal values as much in voltage as in wavelength and, after a certain time of operation, it auto-disconnects due to excessive temperature until cool again. As additional fact worth noting that, by raising its temperature can heat the sample to be analyzed, so it must be taken into account this effect when analyzing the results because the fluorescence is temperature dependent. Therefore, in tests was controlled repeatedly the temperature of the samples, using a non-contact thermometer.

Although this is not the only factor affecting the fluorescence, it is that we had more into consideration, since increasing the temperature decreases the emission.

Other factors to be taken into account in subsequent tests will be in regard the nature of the compound, viscosity (the higher viscosity, higher fluorescence) acidity level (pH) or presence of oxygen. All these factors have more influence and variability when samples are analyzed in the wild, not in the lab

- Another source used to be subjected to analysis in this paper is a low-power laser (5mW) and emitted light which is within the near ultraviolet. In this case, and in order to observe the effects of a wavelength with less energy 405 nm are used, since this type of lasers are on the market at a low cost (Figure 5.). The light thus generated, in contrast to the other light sources, has a high directivity, which gives a good response. Another advantage is the ability to emit pulsed light to observing the decay time, as was done with the aforementioned assembly (Figure 3.).

Figure 5. Ultraviolet laser @ 405nm

- Finally measurements have been performed using UV-LED as a light source emitting in the vicinity of 365 nm (Figure 6.). While typical use value is 350 mA, it can supports more than 700 mA during peaks, so pulsing the light with a low duty cycle, is possible to get better answers. For this purpose a power LED driver was used, which allows to be configured for digital pulse-width modulation (PWM) dimming operation using a digital PWM input signal. It can also be adjusted to feed more than one LED. In our case, the measurements were made with two LEDs

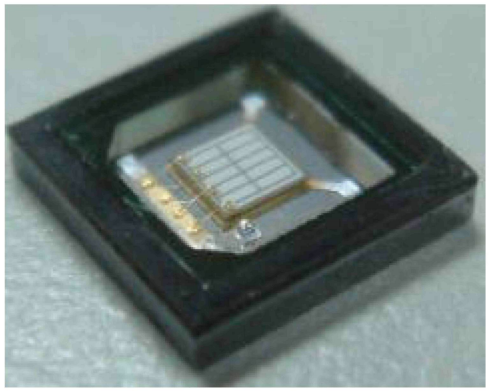


Figure 6. Ultraviolet LED @ 365nm

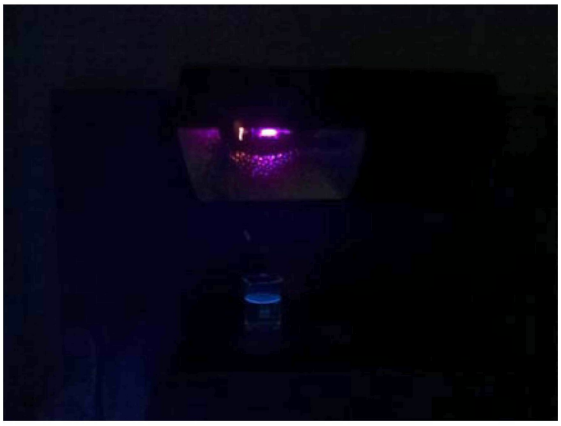


Figure 7. Hydrocarbon sample fluorescence under the effect of a UV bulb.

C. *Spectrometer*

To detect the emitted wavelengths, was used a spectrometer with 2048 pixel CCD detector, a grating ranging from 200 nm to 1400 nm. The effect of fluorescence occurs at wavelengths higher than those of the source, therefore isolate the sensor from the source to avoid coupling between them is desirable, so that this specific spectrometer meets this objective. The resolution is 2.4nm with a 50µm slit. It is important to receive as much as possible light intensity, therefore the optical fiber was used to collect light from the sample under test and carry to the spectrometer, had a quite remarkable thickness, considering that was flexible enough to perform a comfortable manner the assembly but not break. It was determined that the fiber of 600 µm was in our case the most appropriate.

III. RESULTS

We proceeded to take measurements in the laboratory with different and varied hydrocarbons that may be present in inland waters. In this article and as example, different fluorescence are shown, with diesel fuel, gasoline and car lubricating oil (TABLE I.). It has remained the same scale in the graphs of the sources of excitation at 365 nm, in order to compare results. In the case of the laser, given the results, the scales are very different. Using a Pyrex beaker filled with water and with a sheet of different types of hydrocarbons, was obtained initial reference patterns to detect contaminants. In order to attempt to obtain a standardized response, there was a thick and uniform deposition thickness of 1mm and a fixed distance of 12 cm between the water and the light source (this distance is used because of its widespread use in monitoring stations currently in operation).

In this study we have analyzed two types of gasoline with different octane ratings, two common types of diesel (which have different additives, being able to make changes in the spectral response) present in the gas stations, and diesel B for agricultural vehicles and other uses such as heating boilers. Additionally motor oil samples were introduced, as it is also likely to appear in the aquatic environment, being highly polluting. Although in this first study is more important the detection, these results can be useful for exact identification of pollutants in future developments where post-processing will be more elaborate. In the measurements presented here, simply a Cauer-type filtering has been applied, (as it seems to be working better for this type of response) to avoid excess noise shown in the output.

In view of the results and comparing them with others obtained with other light sources seem to suggest that the frequency of the excitation determines the result in the output.

In the obtained spectra with the bulb is clearly visible the heating effect mentioned above, in the form of blunt peak at low frequencies. Although this effect is irrelevant, is shown to be within the range of wavelengths shown for other light sources.

In this respect the other results, the spectral responses appear quite distinct mark of each of the compounds, although it is necessary processing thereof. More ambiguous results are obtained with the laser source, so it should further study with this device. With the 365nm light sources are similar spectra, typical for each pollutant.

The response includes the entire wavelength range of the receiver, allowing verifying that fluoresces with relative ease when a 365nm excitation is used, being it clearly differentiated with uncontaminated sample.

Pollutants may be present individually or in combination with fuel, so later this work will search patterns with mixtures in different proportions. These oils, although less volatile, have also a response easily obtained, as shown in TABLE I. . In this case we see a concentration of the answer in a narrower frequency range than in the diesel, although it seems that can be characterized and differentiated with a easy processing as a simple correlation.

In a later step, we pretend to make a mounting for the continuous measurement, to verify correct operation with circulating water (Figure 8.).

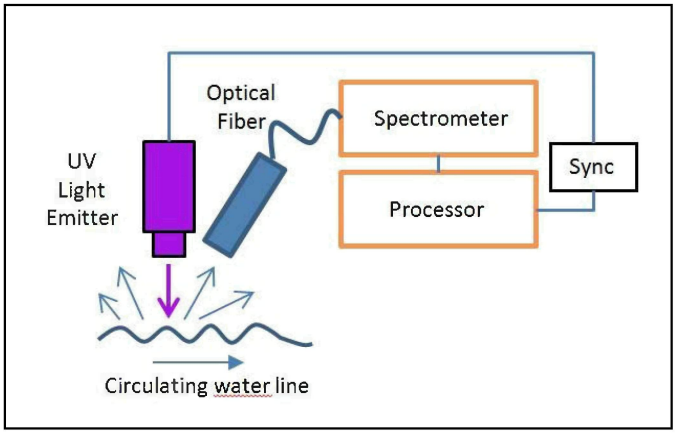
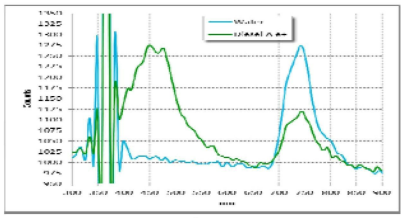
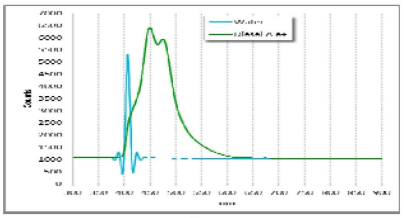
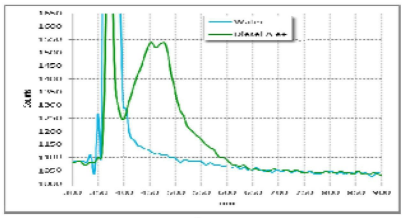
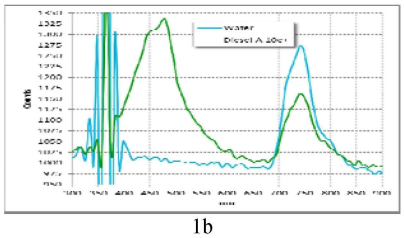
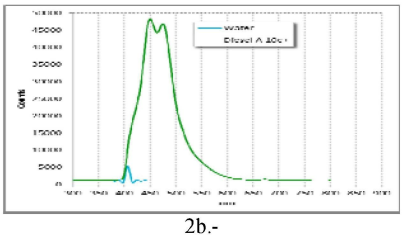
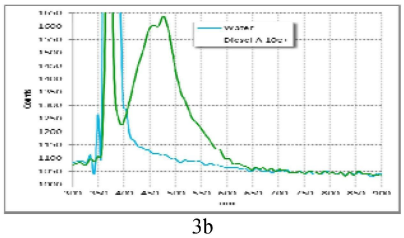
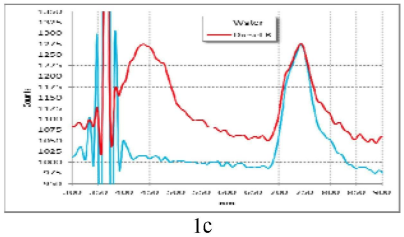
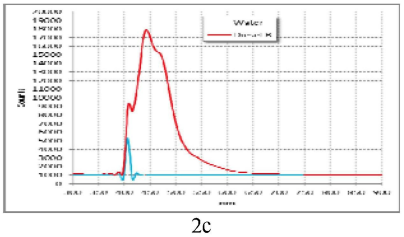
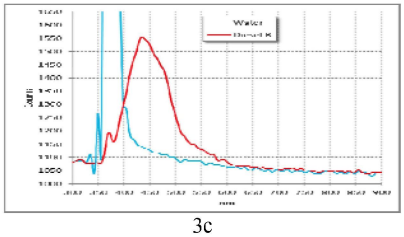
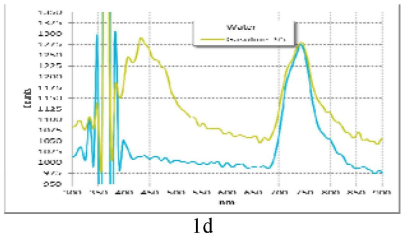
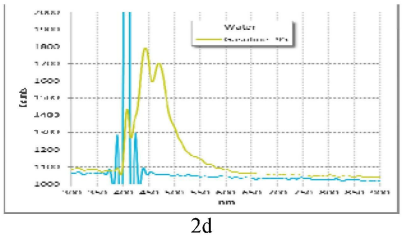
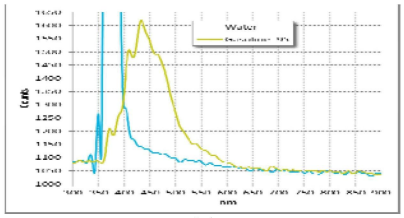
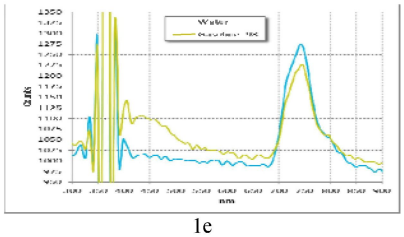
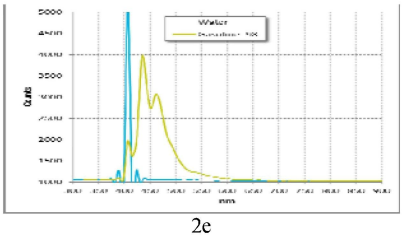
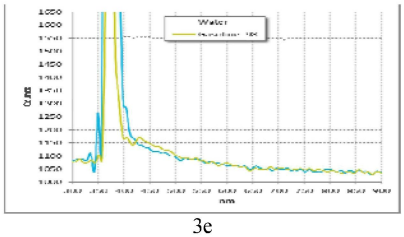
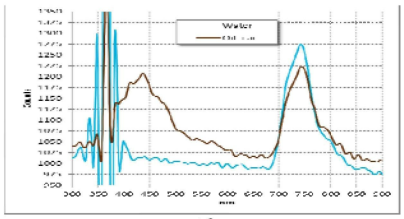
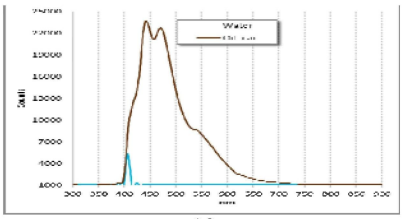
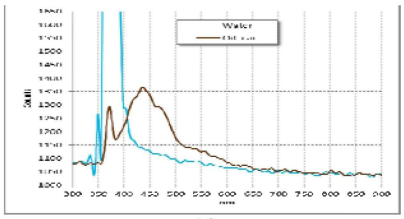


Figure 8. Mounting for continuously measuring

In this case for a closed water circuit, subjected to a mild current, fluid motions exist, altering or modifying the previous results obtained in static. This assembly will be an intermediate step toward the field measurements and the results can be very useful to optimize the positions of the source and the receiver, or even different algorithms that can be employed.

TABLE I. SPECTROMETRIC RESPONSE WITH DIFFERENT SOURCES.

Hydrocarbon Sample	UV Sources		
	UV Bulb (365nm)	*Laser Diode (405nm)*	*UV LED (365nm)*
Diesel A e+	 1a.	 2a	 3a
Diesel A 10e+	 1b	 2b.-	 3b
Diesel B	 1c	 2c	 3c
Gasoline 95	 1d	 2d	 3d
Gasoline 98	 1e	 2e	 3e
Oil Car	 1f	 2f	 3f

IV. CONCLUSIONS

In view of the obtained results, the development of a control system to detect the presence of hydrocarbons in inland waters is possible, at least to a first approximation, measuring and using materials and components much cheaper than those used for ocean waters. The test-bench mounted to this purposes where we could vary incidence and reflection angles, as well as distances and light sources, have been effective to carrying out the measures presented. A very important part is the section concerning the acquisition and processing of data. It is possible a simple processing which can be done by software and devices that do not consume much power and not many hardware resources. We are currently working under the MatLab™ platform developing a program that takes *n* samples per second and execute the calculations described before in quasi real time.

Regarding the light sources used in the prototype proposed, LEDs are best suited for this purpose because they combine ease of use, ability to generate pulsed light and relative low cost. The laser light provides better responses in terms of light intensity, which facilitates the depths sample calculation and decay times, but this must match the reflected beam with the detector, and this fact does not always occur in continuous water flow. This can be solved by making a large number of samples, but there is a risk of no response in many of them.

To the final test we have, in collaboration with the Ministry of Agriculture, Food and Environment, the possibility to use automatic warning stations deployed at several strategic points (these stations belong to the project called SAICA, developed to continuous monitoring of the water quality in rivers. See Figure 9.).

Figure 9. Automatic warning station.

These stations have, among others, temperature and pH sensors, so these measures could be eventually harnessed and used to corroborate or improve the results obtained with the prototype presented.

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